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# NICOTINE and TOBACCO WASTE

*By*

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## PROPERTIES OF NICOTINE AND VALUE AS AN INSECTICIDE.

Nicotine is a colourless liquid alkaloid of specific gravity 1·01, and boiling point 246·7° C. It is very soluble in water, forming a powerfully alkaline solution. It is a mon-acid base, and may be titrated against standard acid, using lacmoid or iodeosin as indicator. It may be separated from a strong solution by the addifion of solid caustic soda or potash, which causes the liquid to form two layers. The nicotine may be obtained from the upper layer by distillation in a current of hydrogen or coal gas. As thus obtained from a commercial 40 per cent solution, it is a colourless liquid, which turns yellow on exposure.

Investigation shows that a solution of 1-1½ ounces of 95 per cent nicotine per 100 gallons of water has a deadly effect upon many insect pests, such as aphids, thrips, apple-suckers, larvæ of winter moths, and most young caterpillars. It does not injure the most tender foliage, and may be mixed with other sprays, such as lead arsenate or Bordeaux mixture, without impairing its insecticidal value to any great extent. Mixed with these, or alone, a 0·05 per cent nicotine solution is sufficiently strong to kill plant lice. In a spraying guide prepared by the Kentucky Tobacco Product Company, the spray recommended is made by diluting one part of 40 per cent solution with 800 to 2,500 parts of water, and varie[illegible] nature of the insects and parts of the plant attacked.

The [illegible]gth (0·05 per cent) has also proved effective when a n[illegible]olution is used as a sheep dip, although 0·07 per cent is required by the Bureau of Animal Industry. For this purpose it has no equal, destroying the sheep-scab and mite, and also killing the tick and louse. It does not affect the wool in any way, beyond a slight discoloration, easily removed by rain or by washing. Its use as a sheep dip is approved by the United States Government. It was formerly supposed to be necessary to add sulphur to such dips, but this has been proved superfluous.

In the proportion of one-fifth ounce of vapour to 2,000 cubic feet of air, free nicotine furnishes a strong fumigator for hen-houses, etc.

Comparative tests show that nicotine sulphate is nearly as effective an insecticide as a solution of free nicotine of the same strength; but nicotine is cleaner to handle, and free from nauseous or injurious constituents.

Nicotine is found in the tobacco plant, free and combined with malic and citric acids. Water dissolves both the free and combined nicotine. Though easily extracted, it is difficult to concentrate and purify, and is therefore expensive. The wholesale price at Louisville, Kentucky, in November, 1917, was:—

NICOTINE SULPHATE.

| Weight of solution. | Strength of solution. | Price per lb. of nicotine. |
|---|---|---|
| ½ pound | 40 per cent | $3 00 |
| 10 pounds | 40 " | 2 25 |

FREE NICOTINE SOLUTION.

| | | |
|---|---|---|
| ½ pound | 40 per cent | 3 80 |
| 8 pounds | 40 " | 2 50 |

In smaller quantities the price is much higher. The retail price of 1 ounce of Graselli nicotine sulphate of 15 per cent nicotine content obtained by the writer was 40 cents, corresponding to $42.66 per pound of nicotine.

## ORIGIN OF INVESTIGATION.

The present investigation originated in a recommendation of Dr. Hewitt, Dominion Entomologist, that the Honorary Advisory Council for Scientific and Industrial Research should take up with the tobacco manufacturers of Canada the question of the manufacture of nicotine sulphate from their tobacco waste. In this connection Dr. Hewitt says:—

"Nicotine sulphate has been found to be the most valuable insecticide for the destruction of sucking insects, such as aphids or plant lice, and we are recommending its use on all occasions. As these insects are very prevalent and destructive in all parts of

Canada and to all kinds of crops, there should be in time a large demand for this product, which has only been on the market for a comparatively few years; and it is only during the last three or four years that we have been recommending its use; but there is undoubtedly a great future for it, if people can only secure it. Its high price prohibits the extensive use it should have. About two years ago, in order to reduce its price to Canadian fruit-growers and others, we had the duty removed; but even when admitted on a duty-free basis its price is still high, being about $2.50 per two-pound tin of 40 per cent nicotine sulphate. Although it has only been on the market a few years, the quantity of nicotine sulphate imported into Canada during the fiscal year ending March 31, 1916, was 15,314 pounds, valued at $13,618. All this came from the United States.

"At the present time thousands of pounds of unused tobacco resulting from the manufacture of cigars, etc., are wasted in Canada.

"I am strongly of the opinion that a very determined effort should be made to induce the tobacco manufacturers to take up the manufacture of nicotine sulphate as a by-product, in view of the growing need of this material in connection with the protection of our crops. Even if they sold it at the same price as the American product, we should at least have the satisfaction of knowing that it was being manufactured in Canada".

The matter was referred to Dr. Ruttan, Chairman of the Chemical Committee of the Council, who sounded two large Canadian companies, the Imperial Tobacco Company and the Tuckett Tobacco Company, on the subject. While they were sympathetic, they did not seem to be inclined to undertake an investigation. Sir Mortimer Davies, of the former company, stated that they had approximately 500,000 pounds of stems and waste available for nicotine production at from $15 to $30 a ton of 2,000 pounds.

Mr. J. D. Ambrose, of the Tuckett Company, stated that their Virginia tobacco waste was being exported to Europe at 1½ cents a pound, and their other stems shipped to Detroit at $10 a ton. He said:—

"With the quantity of stems and dust we produce, it would be quite unpractical for us to attempt to manufacture insecticides or fertilizing material, as the extractable or soluble parts of tobacco stems are only a very small percentage. Personally, I have been

most anxious to see our stems utilized in Canada, either for the manufacture of insecticides or fertilizer, and I take the liberty of suggesting that, if your Council took the matter up with the manufacturers of these articles, there would be no difficulty in obtaining the tobacco companies' by-products at reasonable prices."

Dr. Ruttan endeavoured to interest chemical companies in the matter, and also to secure information concerning the nicotine contents of tobacco waste, and the methods of extraction. This proved difficult, as there are comparatively few companies manufacturing nicotine, and their processes are secret or patented. It was therefore decided to secure the desired information by investigation.

The work was carried on at the University of Toronto, under Prof. W. Lash Miller, who also gave valuable assistance in revising this report.

## THE WASTE ON THE PLANTATION.

Attention was first directed to the waste on the plantation. This, according to Mr. J. A. McDougall, managing director of Walker Sons, of Walkerville, consists of the stalks and roots. In communication with Mr. F. Charlan, Chief of the Tobacco Division of the Canadian Department of Agriculture, as to the feasibility of extracting nicotine from this material, attention was directed to the following tables:—

TABLE 1.—Stalks. Weight of nicotine in 100 of dry material.

| Bark | | Wood | | Centre | |
|---|---|---|---|---|---|
| " | 0·46 | " | 0·10 | " | 0·30 |
| " | 0·60 | " | 0·15 | " | 0·56 |
| " | 1·37 | " | 0·21 | " | 0·82 |
| " | 2·12 | " | 0·25 | " | 1·71 |
| " | 1·20 | " | 0·65 | " | 1·90 |
| " | 1·75 | " | 0·18 | " | 1·63 |
| " | 1·90 | " | 0·45 | " | 2·30 |
| " | 2·02 | " | 0·22 | " | 1·86 |
| " | 2·30 | " | 0·51 | " | 2·20 |
| " | 0·70 | " | 0·19 | " | 0·16 |
| " | 0·78 | " | 0·54 | " | 0·59 |
| " | 0·95 | " | 0·80 | " | 0·84 |
| " | 1·08 | " | 1·30 | " | 1·74 |
| " | 0·78 | " | 0·78 | " | 0·78 |
| " | 0·95 | " | 0·92 | " | 0·95 |
| " | 1·75 | " | 1·74 | " | 1·82 |
| | 20·71 | | 8·99 | | 20·10 |
| Average | 1·29 | | 0·56 | | 1·25 |

TABLE II.—Roots. Weight of nicotine in 100 of dry material.

| —— | —— | —— | —— | —— | Average. |
|---|---|---|---|---|---|
| Pivot | Bark | 3·33 | | | 3·33 |
| | Wood | 0·36 | | | 0·36 |
| Secondary Roots | Bark | 4·25 | 3·10 | 3·90 | 2·85 | 3·52 |
| | Wood | 0·60 | 0·35 | 0·45 | 0·54 | 0·48 |
| Hair | | 1·81 | 1·74 | 1·50 | 1·27 | 1·58 |

TABLE III.—Weight of nicotine in 100 of dry material.

| —— | Leaves. | Stalks. | Roots. | Suckers |
|---|---|---|---|---|
| July 14 | 0·34 | 0·03 | 0·45 | |
| Aug. 9 | 3·12 | 0·61 | 0·69 | 1·04 |
| Sept. 18 | 4·79 | 0·52 | 0·64 | 1·27 |
| Nov. 4 | | 0·47 | 0·53 | 1·04 |

Mr. Charlan's conclusions from these tables are as follows:—

"The experiments in table No. I represent fairly well in my opinion, what we can expect from the average Canadian tobaccos. There are large variations in the nicotine content from the same parts of the stalks. This can also be expected in Canada, as a large number of varieties of tobacco are grown in this country for commercial purposes.

"It can easily be seen that most of the nicotine content of the stalk is contained in the bark and in the centre, the woody part containing only a small proportion of nicotine.

"Experiments carried on in Connecticut have shown that for a total amount of 1,270 pounds of dry stalks per acre the amount of nicotine that can be extracted is only 6·6 pounds, which means something like 0·5 per cent. Another series of experiments has given for 1,328 pounds of dry stalks 8·8 pounds of nicotine, which is a little higher; but in every case the total amount of nicotine that can be extracted from the stalks is very low.

"In the roots we find (table II) a comparatively high proportion of nicotine in the bark, the woody part being very low in alkaloid. The hair yields something like 1·58 per cent of nicotine;

but I think that in practice the hair will never reach the manufacturer. The proportion of bark to the wood being very small, it is easy to conclude that the total amount of nicotine that can be extracted from the roots is rather low. Table III gives this total obtained from another series of experiments.

"The yield per acre in dry stalks can be figured, as already stated, at 1,270 to 1,350 pounds. Some varieties of tobacco yield a much heavier stalk, but they are transplanted at wider distances, and the number of plants per acre being smaller, we can figure on the same total yield in dry matter."

Thus, according to this authority, the waste on the plantation would not prove a very profitable source of nicotine. Prof. E. Pannain, of the Royal University of Rome, found 0·16 per cent in the roots and 0·19 per cent. in the stalks.

Analyses of stalks made in Connecticut show the following nicotine content:—

| | Fresh. | Water free. |
|---|---|---|
| | per cent. | per cent. |
| Cut unripe Aug. 22 | 0·07 | 0·52 |
| Cut ripe Sept. 7 | 0·09 | 0·69 |

On this basis, a calculation in the same report shows the yield of nicotine per acre of stalks to be cut unripe, 6·6 pounds; cut ripe, 8·8 pounds.

This is about what may be expected from Canadian stalks, as indicated by an analysis of stalks furnished by Walker Sons, Walkerville. The stalks, which were allowed to dry in the air, gave 0·57 per cent nicotine (table IX). The Henderson Tobacco Extract Works found 0·8 per cent in dark Kentucky stalks.

It appears that, to an established industry, finding difficulty in securing raw material, this might prove a profitable source of supply. In support of this view, Chuard and Millet found that the waste incidental to the Swiss tobacco culture-tops, axillary buds or sprouts, stalks, roots and shoots, contains a notable quantity of nicotine; and, treated in the green state, to prevent loss, forms an important commercial source. They also found that the

nicotine content of the stalks depends on their treatment after the leaves have been stripped from them. If left in the ground, and sodium nitrate added as a fertilizer, the amount of alkaloid extractable is increased by 77 per cent.

## THE GROWING OF TOBACCO FOR NICOTINE EXTRACTION.

Mr. Charlan's letter, referred to above, ends as follows:—

"In my opinion, the only practical solution for the establishment in the country of the nicotine industry would be the growing for that special purpose of certain varieties of tobacco with a high percentage of nicotine. These varieties are not suitable for smoking purposes. They will have to be grown in those parts of Canada where the climate is comparatively warm and not too damp. Being devoted only to the production of nicotine, they could be grown at smaller expense than the average crop. The total amount of nicotine which can thus be produced per acre has been estimated by some experimenters at about 100 pounds. I think it would be safe to figure on 75 pounds to 120 pounds per acre, according to the season. In a normal year, rather warm, but with enough rain to keep the plant growing well, the amount of nicotine will be high. If the season is too dry and the growth of the plant is checked, the total amount will be small. It will also be small if the season is cool and wet. Under the climatic conditions of the tobacco-growing districts in Canada the growing of tobacco for nicotine will then always be risky. Still, if we figure on the prices at which nicotine can be sold, let us say $2 per pound to be very conservative, we see that 72 pounds per acre means a money return of $150. This, however, has not been considered by the experimenters sufficient to cover the expenditure involved by the growing of the plant and the cost of extraction. I must say that, in most cases, the varieties of tobaccos which have been selected for the experiments were not very good nicotine yielders. The use of the Italian Herbasentas will probably enable the growers to get a yield of 120 pounds to 125 pounds of nicotine per acre, providing weather conditions are favourable. This, in my opinion, should prove a paying proposition."

Considerable experimental work has been carried on at South Eastern Agricultural College, Wye, Kent, England, to determine

the best varieties of tobacco to use, conditions of growth, methods of curing, etc., in order to obtain a maximum yield of nicotine. The results are embodied in a pamphlet issued by the college. A summary of results obtained is given herewith:—

*Effect of the soil.*—The greatest percentage of nicotine was obtained in plants grown on rich hop-garden soil. Clay loam yielded about 1 per cent less, and alluvial soil gave the lowest yield.

*Effect of manures.*—Farmyard and artificial manures combined yielded the best crop, 155 pounds nicotine per acre. The former alone yielded 131 pounds. Nitrate of soda alone yielded 120 pounds, and the addition of kainit did not increase the yield. Green manure yielded only 87 pounds.

*The best distance apart.*—It was found that when the plants were placed close together (18 by 26 inches) although the percentage of nicotine was diminished the total yield per acre was greatest, being 196 pounds when *Nicotiana rusticana* was used.

*The best height of topping.*—Plants topped at 12 leaves were found to yield the greatest percentage of nicotine and the greatest amount per acre.

*The best time to cut.*—It was found that the nicotine content increases by about 0·5 per cent, if the crop is left to mature; but, if left very late, there is a slight loss.

*The most suitable variety to grow.*—Some varieties of *Nicotiana rusticana* produced the greatest yield. *Rustica* (Ireland) produced 8·32 per cent.

*The best method of drying.*—Natural drying, by tying the plants bodily on sticks, was found best. They should be finished off with a little artificial heat.

*Cost and returns.*—The total cost of growing tobacco in 1911 was at the rate of £27 per acre. On twenty-three different plots a yield at the rate of 150 pounds per acre was obtained, costing 3s. 7d. per pound. In 1911 the yield was about two and a half times as great as in 1910, due to the different seasons. A yield of from 70 to 150 pounds per acre may be expected, costing from 3s. to 8s. 6d. per pound, compared with the market price of 15s. per pound.

Work similar to the above has also been undertaken in the United States. In this connection, Mr. W. W. Garner, Physiologist in charge of Tobacco Investigations of the Bureau of Plant Industry, in a letter dated November 9, 1917, says: "Although we have done considerable work relating to the production of nicotine from tobacco for insecticidal purposes, with special reference to the development of types or varieties with high nicotine content, we have not as yet published anything on the subject".

## THE PREPARATION OF NICOTINE EXTRACTS FOR USE ON THE SPOT.

Experiments were conducted to enable fruitgrowers and farmers to grow their own crop of tobacco from which they could manufacture their own insecticide and sheep wash. This would greatly

reduce the cost. But a simple and easy method of extracting the nicotine is essential to such a result.

Experiments to this end were carried out by Mr. Edwardes-Ker in the chemical laboratory of the South Eastern Agricultural College, and the results of these are contained in the pamphlet referred to above. He used tobacco leaves, and found that water at ordinary temperatures would extract 96 per cent of the nicotine. A somewhat better result was obtained with warm water. Water above 60 degrees Centigrade should not be used, as it causes volatilization of nicotine. The following directions for preparing a 0·075 per cent solution are given:—

"For every acre to be sprayed,take 100 pounds air dried tobacco leaves, stir thoroughly with 100 gallons water (warm, if possible) and allow to stand for one day. Run the extract from the leaves, and extract the latter twice again, similarly with 100 gallons of water".

This gives a 0·075 per cent nicotine solution from tobacco containing about 2·40 per cent nicotine. Analysis of Canadian tobacco showed a nicotine content of 2·70 per cent (table IX). Thus, treated according to the above directions, it would yield about the proper strength of solution. Extracts prepared as above were found to ferment if kept a few days. A small quantity of formalin prevented this.

Another plan for the preparation of tobacco extracts consists in purchasing the scrap or stems from tobacco factories and utilizing them instead of home-grown tobacco. This was investigated at the Virginia Agricultural Experiment Station with Virginia tobacco waste. The following directions for making an extract are given:—

"If the fruitgrower has a lime-sulphur cooker, he can soak the tobacco in water and then turn in the steam. As soon as the solution reaches the boiling point, the steam should be shut off and the barrel or kettle allowed to cool, and the decoction strained to free it of the stems or leaves. If practicable, he may use some means to press out the refuse. An open kettle can be used, but the yields of nicotine will be less, owing to volatilization and evaporation.

"From our experiments we believe that for all practical purposes tobacco extracts can be made on the farm with nearly as good results as cooking with steam, simply by allowing the tobacco or stems to soak twenty-four hours, and strain".

Table IV gives the number of pounds of tobacco necessary to yield 100 gallon extracts containing 0·06 and 0·05 per cent of nicotine, respectively, assuming that 75 per cent of the nicotine is extracted. According to this bulletin, these strengths are sufficient to kill plant lice. The calculations were made from my analyses on the basis of a similar table contained in the bulletin.

TABLE IV.

| Kind. | Where from. | Per cent nicotine. | No. lb. per 100 gal. necessary to make nicotine solution. | |
|---|---|---|---|---|
| | | | per cent 0·06 | per cent 0·05 |
| Canadian stems | McAlpine Tob. Co., Toronto | 1·06 | 66 | 55 |
| Havana stems | Andrew Wilson Co., Toronto | 1·05 | 66½ | 55½ |
| Connecticut stems | Andrew Wilson Co., Toronto | 1·17 | 60 | 50 |
| Mixed Canadian and Virginia stems | Imperial Tob. Co., Montreal | 0·73 | 96 | 80 |
| Wisconsin stems | Tuckett's, Hamilton | 1·15 | 61 | 50 |
| Tobacco dust No. I | Imperial Tobacco Co., Montreal | 1·55 | 45 | 37½ |
| Tobacco dust No. II | Imperial Tobacco Co., Montreal | 1·75 | 39 | 32½ |
| Cigarette cuttings | Imperial Tobacco Co., Montreal | 0·78 | 89½ | 75 |
| Canadian scrap | McAlpine Tobacco Co., Toronto | 2·41 | 29 | 24½ |
| "Bachelor" scrap | Andrew Wilson Co., Toronto | 1·33 | 52½ | 44 |
| Canadian stalks (dry) | Walker & Sons, Walkerville | 0·57 | 130 | 103 |
| Sumatra stems | Tucketts, Hamilton | 0·77 | 91 | 76 |

The Virginia Agricultural Experiment Station tested the decoctions they prepared and obtained good results.

It is calculated that with stems at $20 a ton, a home-made spray will cost $1 per 100 gallons, as compared with $1.20 for Black Leaf 40. After the extraction of the nicotine, the stems are worth $10 a ton as fertilizer.

With the higher nicotine content and lower price of Canadian stems, the cost of nicotine in Canada would be considerably less than that derived from Black Leaf 40. The stems would have a much higher value as fertilizer at the present time; but their value during normal times may have been overestimated, as my experi-

ments show that a large amount of fertilizing material is extracted with the nicotine (over one-half pound per 10 pounds of stems).

The Kentucky Agricultural Experiment Station has investigated the preparation and use of home-made tobacco decoctions for dipping sheep. As a 0·05 per cent solution has been proved effective for sheep dipping the amounts of tobacco indicated in table IV should also serve for the preparation of sheep dips. The following table (V) and directions are reprinted from Bulletin 143 of this Station to supplement the above:—

TABLE V.—Quantities of Tobacco to make Sheep Dip.

| No. | Kind of Tobacco. | Per cent Nicotine. | Pounds per 100 gals. of water. |
|---|---|---|---|
| 1 | Dark tobacco leaves | 2·5-4 | 21 |
| 2 | Sweeping of dark tobacco | 2·75-3·00 | 23 |
| 3 | Dark Western Kentucky stems | 1-1·2 | 60 |
| 4 | Dark Western Kentucky stalks | 0·8 | 105 |
| 5 | Burley leaves | | 24 |
| 6 | Sweepings of Burley tobacco | 2·25 | 26 |
| 7 | Burley stems | 0·6-7 | 75 |
| 8 | Burley stalks | | 125 |

NOTE.—Percentages for 1, 3 and 4 above are on water free basis; others are not.

The directions for using these quantities to make a dip are:—

"The part of the tobacco plant used for the decoction is soaked in lukewarm water for twenty four hours in a covered pot or kettle. This mixture is then heated to the boiling point for an instant, and allowed to soak again for an hour or two.

"The contents are then strained under considerable pressure so as to get out as much of the ooze as possible, and diluted with sufficient water to make 100 gallons. The proper amount of sulphur, 16 pounds, is then added and the entire mixture thoroughly stirred. If the water added is hard, it should be softened by lye or sal-soda, and warm enough so that the mixture complete will read at a temperature of 100 to 105 degrees Fahrenheit. During the dipping, the contents of the vat must be thoroughly stirred from time to time. As tobacco dips deteriorate quite rapidly, a fresh solution should be made up when the sheep are dipped the second time, which is usually from ten to fourteen days after the first dipping".

It is recommended to dip a few sheep at the beginning and wait a little while to see the effect, as too strong a solution makes the sheep sick.

Attention is again called to the fact that later experiments in the same station proved that the addition of sulphur is entirely unnecessary.

## NICOTINE FROM TOBACCO WASTE.

To quote Mr. F. Charlan again:—

"For practical purposes one must look for the supply of nicotine to what is known in the tobacco trade as waste-tobacco products. These include tobacco stems, when no use is found for them in the factory. Some tobacco leaves are used without being stemmed, but the larger proportion is stemmed in order to give a better appearance to the finished product. Some of the stems, however, after being treated, and sometimes flattened, find their way into the cheap brands. These stems contain an average of about 1 per cent of nicotine, which is rather low. They can, however, very easily be treated for the extraction of nicotine. At the present time they are mostly used for the extraction of potash, the proportion varying with the variety of tobacco and the type of soil. The best possible utilization of these tobacco stems, as long as the price of potash remains high, will be the extraction of both nicotine and potash, the residue being used as fertilizer, as it will still contain a large proportion of nitrogen".

The primary object of the investigation was to determine the feasibility of extracting nicotine from this waste on a commercial scale. For, while the manufacture of nicotine solutions on the spot is the cheapest method of obtaining them, the majority of farmers and fruit growers would probably prefer to buy concentrated standard solutions if at all reasonable in price. The investigation naturally divides itself into two parts: (1) determination of the nicotine content of the waste; (2) investigation of method of extracting the nicotine.

### ANALYSES OF CANADIAN TOBACCO AND WASTE.

After investigation, it was decided to use the silico-tungstic acid method of analysis as suggested by Bertrand and Javillier

and investigated by R. M. Chapin. However, it was found possible to secure only 1 ounce of the expensive silico-tungstic acid required. This was used for testing the method, and for analyses 1, 2, 3, table VI; analyses 4 and 5, table VIII; and the analyses of casing liquor and Canadian tobacco, table IX.

Upon the supply failing, attention was directed to the methods of preparing the acid. It was noted that Bertrand and Javillier used the potassium salt instead of the acid. In a general way the directions of Dreschsel were followed to the point where sodium silico-tungstate was obtained. This was then tested and found to give a distinct precipitate with 1 part of nicotine in 80,000. The re-agent was next tried on tobacco and compared with silico-tungstic acid, with the following results:—

| Nicotine found in | Using silico-tungstic acid. | Using Re-agent. |
|---|---|---|
| | per cent | per cent |
| Canadian tobacco | 2·70 | 2·66 |
| Connecticut stems | 1·17 | 1·12 |

Thus the re-agent gives results somewhat lower than the pure acid.

This difference is not as great as between many other methods of analysis tried on the same specimen. Tingle and Ferguson obtained the following percentages for the same specimen by three different methods: Toth, 1·89 per cent; Kissling, 1·74 per cent; and Tingle and Ferguson's polarimetric method, 2·27 per cent. Three analyses of the same solution of nicotine sulphate by different chemists are:—

| | per cent |
|---|---|
| Kentucky Experiment Station | 42·21 |
| Bureau of Animal Industry | 40·79 |
| Manufacturers Chemists | 39·20 |

Ellett and Grissom found the Kissling method unreliable for dilute aqueous solutions. So it was decided to use the sodium silico-tungstate re-agent in preference to other methods. This re-agent has the advantage of being cheaply and easily prepared and appears to give results accurate enough for commercial work. It

is especially valuable in the investigation and control of manufacturing processes.

The re-agent was prepared as follows:—100 grams of sodium tungstate ($Na_2 WO_4$) was boiled with 400 cubic centimetres water and 70 per cent nitric acid added till the solution was neutral to litmus (about 24 cubic centimetres). The resultant solution was boiled with excess of gelatinous silica till no precipitate was formed with hydrochloric acid. It was then filtered and diluted to 1000 cubic centimetres with distilled water. The gelatinous silica was prepared by heating a mixture of ground silicate (glass or feldspar) and fluorspar with sulphuric acid, passing the silicon fluoride obtained into water, filtering and washing.

Directions for analysis by the silico-tungstic method or with this re-agent are briefly as follows:—

Weigh the powdered tobacco or extract and place in a 500 cubic centimetre round-bottomed flask. Add 1 to 1½ grams of paraffin, a few small pieces of pumice, and about 10 cubic centimetres of a 30 per cent solution of sodium hydroxide. Then steam-distil until the distillate gives no opalescence with a drop of silico-tungstic acid or re-agent followed by a drop of 1 to 4 hydrochloric acid. Dilute the distillate (usually about 300-600 cubic centimetres) to a convenient volume, say 500 or 1000 cubic centimetres, and filter. Transfer an aliquot amount (say 100 cubic centimetres) to a beaker and add 3 cubic centimetres of hydrochloric acid (1 to 4) for each 100 cubic centimetres of liquid, or enough to render acid. Add silico-tungstic acid, or the re-agent, till no further precipitate forms. If the re-agent is used the precipitate does not become as completely crystalline as that formed by the silico-tungstic acid. Heating to about 60 degrees hastens the change to a filterable form.

Stir and let stand for eighteen hours. Filter, wash with cold water containing 1 cubic centimetre concentrated hydrochloric acid per litre. Test filtrate to prove excess of acid or re-agent. Transfer to a weighed crucible, carbonize, burn off the carbon at as low a temperature as possible, and ignite over Bunsen burner, finishing with 5 to 10 minutes over a blast lamp. Cool in desiccator and weigh. The weight multiplied by 0·114 gives the weight of nicotine.

Results of numerous analyses of tobacco have shown that the nicotine content in a particular variety varies with the soil, climatic

conditions and method of curing. Dr. W. W. Garner, of the Bureau of Plant Industry, Washington, D.C., says: "Seasonal variation exerts a most marked influence on the nicotine content, so that the average quantity contained in a tobacco may be twice as much one season as another; also the methods of curing will influence the amount contained in the cured product. If sufficient heat is used in the curing to raise the temperature to any great extent, quantities of nicotine are volatilized".

This is illustrated in table VII. Havana seed stems, cured by the priming method, showed a nicotine content of 0·51 per cent green and 0·50 per cent cured; while cured on the stalk they contained 0·87 per cent green and 0·44 per cent cured. Halladay stems in 1909 showed 0·38 per cent green and 0·34 per cent cured; while in 1910 they showed 0·17 per cent green and 0·18 per cent cured. Two specimens of Connecticut stems from the Andrew Wilson Company showed contents of 1·12 per cent and 0·76 per cent, respectively. In making the analyses of stems, etc., no special effort was made to dry them. They were merely spread out and left in a warm dry room for several days. The results are contained in the following table:—

TABLE VI.—My Analyses of Stems

| No. | Variety of Stems | Where obtained. | Per cent nicotine. |
|---|---|---|---|
| 1 | Canadian Burley | McAlpine Tobacco Co., Toronto | 1·06 |
| 2 | Havana | Andrew Wilson Co., Toronto | 1·05 |
| 3 | Connecticut | Andrew Wilson Co., Toronto | 1·17 |
| 4 | Mixed (Can. and Vir) | Imperial Tobacco Co., Montreal | 0·73 |
| 5 | Wisconsin | Tucketts Tobacco, Hamilton | 1·15 |
| 6 | Sumatra | Tucketts Tobacco, Hamilton | 0·77 |
| | | Average | 0·99 |

TABLE VII.—Analyses of Stems by other Investigators.

| By whom analyses were conducted. | Variety of stems. | Per cent Nicotine. |
|---|---|---|
| U.S. Dept. Agr..... | (a) Cured by priming method — | |
| | Havana Seed (1908)— | |
| | Green.. | 0·51 |
| | Cured | 0·50 |
| | Halladay (1909)— | |
| | Green.... | 0·38 |
| | Cured | 0·34 |
| | Halladay (1910)— | |
| | Green... | 0·17 |
| | Cured | 0·18 |
| | (b) Cured on the stalk,— | |
| | Havana Seed (1908) | |
| | Green.. | 0·87 |
| | Cured | 0·44 |
| | Halladay (1909)— | |
| | Green... | 0·45 |
| | Cured | 0·31 |
| | Halladay (1910) | |
| | Green... | 0·22 |
| | Cured | 0·12 |
| Virginia Agr. Expt. Stn. | Virginia from Richmond. | 0·481 |
| | Virginia from Danville.. | 0·609 |
| Prof. E. Pannain, Royal Univ., Rome..... | 1st picking. | 0·46 |
| | 2nd picking | 0·73 |
| | 3rd picking.... | 0·24 |
| | 4th picking.... | 0·33 |
| Henderson Tobacco Extract Works, Henderson, Ky..... | [illegible]t Western Kentucky.. (Water-free). | 1 to 1·2 |
| Kentucky Tobacco Product Co., Louisville, Ky..... | Burley Stems | 0·6 to 0·7 |
| | Dark Stems. | 0·75 to 1·0 |
| | (Not water-free). | |

The last two sets of figures correspond very well with our results for stems from Canadian factories.

TABLE VIII.—Analyses Scrap and Dust.

| No. | Kind. | Where obtained. | Per cent nicotine. |
|---|---|---|---|
| 1 | Tobacco dust | Imperial Tobacco Co., Montreal | 1·55 |
| 2 | Tobacco dust | Imperial Tobacco Co., Montreal | 1·79 |
| 3 | Cigarette cutti..gs | Imperial Tobacco Co., Montreal | 0·78 |
| 4 | Canada scrap | MacAlpine Tobacco Co., Toronto | 2·41 |
| 5 | "Bachelor" scrap | Andrew Wilson Co., Toronto | 1·33 |

TABLE IX.—Other Analyses.

| No. | Kind. | Where obtained. | Per cent Nicotine. |
|---|---|---|---|
| §1 | "Casing" liquor | Andrew Wilson Co., Toronto | 0·01 per cent |
| 2 | Canadian tobacco | Walker and Sons, Walkerville | 2·70 " |
| 3 | Canadian stalks | Walker and Sons, Walkerville | 0·57 " |

§To illustrate the inaccuracy of some methods of analysis, applied to dilute aqueous solutions Toths' method gave about 0·5 per cent, compared with 0·01 per cent by the silico-tungstic acid method.

It may be explained that the "casing" liquor is produced by dipping the leaves in water to soften them before removing the midribs. It was thought that this liquor might contain considerable nicotine as it became dark-coloured by the end of the day. In Wilson & Company's factory about 800 pounds are cased per day, yielding about 1000 pounds of liquor containing about 1½ pounds of nicotine. The solution is not strong enough to be of value as an insecticide and the small nicotine content would not warrant extraction. In a factory casing four or five times as much tobacco per day, the liquor might prove of value to fruit-growers in the surrounding districts. The easiest way and surest to find out would be to try some as a spray.*

The only other waste liquor is produced in connection with the manufacture of chewing tobacco. The leaves are dipped in a decoction to sweeten and flavour them. This in time becomes

*Tucketts of Hamilton, case about 2000 pounds per day.

quite dark, and probably contains considerable nicotine. However, Mr. Spence, Excise Officer at the McAlpine Tobacco Company, and in that capacity connected for twenty years with the tobacco industry, states that the quantity of waste liquor from this source is negligible.

Cuttings, scrap, and dust constitute another waste product. The first two have a value in the tobacco trade which prohibits their use as a source of nicotine. For example, one company gets 12 to 13 cents a pound or $240 a ton, for its scrap. The nicotine content is only 90 pounds per ton worth about $180. The Tuckett Tobacco Company produces only about 500 pounds of dust a year, which could be turned to this use. The dust contains considerable sand, which measurably lessens its nicotine content.

The greatest part of the waste consists of stems. According to Mr. Spence, stems constitute 19 per cent to 20 per cent of the raw tobacco. These are the midribs of the leaves, and are removed either by hand or by machinery. All the stems investigated, except those from the Imperial Tobacco Company, had a fringe of leaf attached, which probably increased the nicotine content.

The analyses given show that the stems from Canadian factories contain sufficient nicotine to warrant their being used as a commercial source. In this connection Dr. E. H. Jenkins, Director of the Connecticut Agricultural Experiment Station in a letter says: "Tobacco stems, I believe, are now frequently treated for the extraction of nicotine".

## THE EXTRACTION OF NICOTINE FROM TOBACCO.

Although there are a number of companies manufacturing nicotine in the United States and on the Continent, it was difficult to find out their methods. Mr. W. W. Garner, of the Bureau of Plant Industry, Washington, in reply to a letter under date of November 9, 1917, said: "We have nothing available dealing with the details of manufacture". Mr. J. K. Haywood, Chief of the Miscellaneous Division of the Bureau of Chemistry of the United States Department of Agriculture, writes: "There is little published information concerning the commercial extraction of nicotine from tobacco stems and refuse. There are two general methods employed, one of which consists in extracting the nicotine from the powdered tobacco stems by an organic solvent such as

gasoline, and subsequent recovery of the nicotine. In the other method the powdered tobacco is submitted to steam distillation, by which process the nicotine is carried over with the steam. In both processes the powdered tobacco is first mixed with a small amount of an alkali such as quicklime, in order to liberate the nicotine. The details of these methods are usually kept secret by the manufacturers, or are covered by patents".

Mr. Alex. Galt Robinson, Vice-President of the Kentucky Tobacco Product Company writes, October 20, 1917:—

"The Kentucky Tobacco Product Company is the largest producer in the world of nicotine solutions, which latter are manufactured under its patent and secret processes, the development of which has cost the company many thousands of dollars. Accordingly, despite our desire to co-operate in every reasonable way with the Canadian Government and with your University, nevertheless we are sure you will at once appreciate that, in the circumstances, the officers of the Product Company would not be justified in divulging its manufacturing method.

"As there are comparatively so few producers of nicotine solutions, no machinery is devised with the special object of equipping a nicotine factory such as would be the case, for example, in a shoe factory. Accordingly, to the best of our information, each nicotine manufacturer is largely dependent upon his own special devices, there being considerable variation in the methods of manufacture now in vogue".

I therefore undertook a somewhat hurried investigation to determine the relative merits of the various methods of extraction. From a study of patents there appear to be four general methods for the extraction of nicotine:

1. Absorption from smoke.
2. Water extraction and concentration or removal from extract.
3. Extraction with hydrocarbon.
4. Steam distillation.

| United States Patents. | English Patents. | |
|---|---|---|
| No. | No. | |
| 1,156,609 | 7071 | May 11, 1915 |
| 12,994 (original No. 899,856) | 2926 | Feb. 15, 1915 |
| 999,674 | 2394 | Feb. 15, 1915 |
| 1,039,987 | 11,460 | May 9, 1910 |
| 1,016,844 | 26,939 | Dec. 11, 1908 |
| 1,055,360 | 23,528 | Oct. 24, 1911 |
| 1,078,427 | 28,085 | Dec. 13, 1911 |
| 1,123,522 | 20,395 | Sept. 14, 1911 |
| 1,146,014 | 11,758 | May 17, 1912 |
| | 20,347 | Sept. 6, 1912 |

## 1. Absorption from Smoke.

In investigating the first method an asbestos-covered iron pipe of length 20 inches and diameter $1\frac{1}{4}$ inches was employed. One end was covered by wire screen and the other was connected to a Liebig condenser which, in turn, was connected to a cylindrical absorption vessel containing sulphuric acid. A filter pump connected to the latter produced the necessary draught; 75 to 100 grams of stems broken into pieces quarter to half inch long were placed in the tube and ignited. They continued burning, and the temperature of the tube and contents became very high. It was thought that the high temperature would distil off the nicotine before there was any likelihood of its decomposition during burning. The results were as follows:—

TABLE X

| No. | Weight of Stems used. | Nicotine content. | Acid used. | Nicotine obtained. | Percentage of nicotine obtained. |
|---|---|---|---|---|---|
| 1 | 100 grams | 1·06 grams | 25cc. 2N | ·260 grams | 24 per cent. |
| 2 | 75 " | ·802 " | 75cc. 2N | ·604 " | 76 " |
| 3 | 100 " | 1·07 " | 50cc. 2N | ·571 " | 53 " |
| 4 | 100 " | 1·07 " | 25cc. 8N. | ·515 " | 48 " |

In No. 1 the liquid obtained was alkaline in reaction, so it was concluded sufficient acid had not been used. In Nos. 3 and 4 the condenser was dispensed with. The product was a dark-coloured liquid, having a strong burnt odour. Considerable tarry matter was deposited on the condenser and absorption

apparatus. The smoke absorption apparatus was far from perfect, and the result of No. 2 seems to indicate that, in cases where the stems are burned for the potash content, it would pay to extract the nicotine by this method rather than let it escape with the smoke. An apparatus for this purpose has been patented, in which the smoke is drawn from the bottom of the apparatus instead of the top, and thus the effect of the heat generated in distilling off the nicotine is not fully utilized. A better absorption is accomplished by means of screens placed in the absorption apparatus to break up the smoke; but these may become clogged with tar, and cause difficulty.

### 2. Extraction with Water or Dilute Acid.

These methods are grouped together because the mode of operation is the same for both. Both were first investigated on a small scale. One hundred grams of coarsely ground stems, containing, by analysis, 1·07 grams nicotine, were placed in each of two flasks, 500 cubic centimetres of water added to one and 500 cubic centimetres of 2 per cent sulphuric acid to the other. Both were let stand for one-half hour, with several shakings.

On the basis of 500 cubic centimetres of solution the nicotine extracted was:—

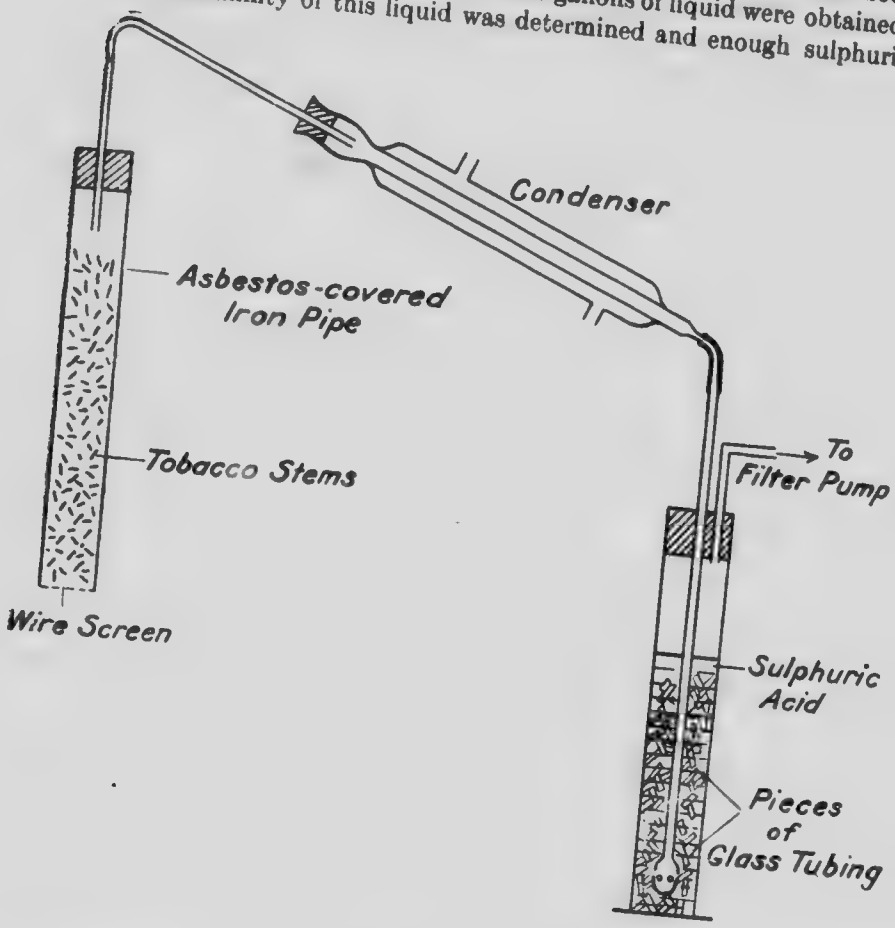
1. From acid extraction 0·8413 grams or 78 per cent.
2. From water extraction 0·7540 grams or 70·5 per cent.

The actual quantities of extract obtained by filtering, without any effort to press out the stems, were 208 cubic centimetres and 200 cubic centimetres respectively.

Water extraction has been tested on stems by Ellett and Grissom who obtained from 37·16 per cent to 77·91 per cent of nicotine present, depending on the temperature of the water and method of extraction. Soaking twenty four hours is recommended. D. R. Edwardes-Ker found that water should extract 96 per cent of the nicotine from finely powdered leaves if used in three successive extractions.

Water extraction was tried on a 10 pound lot to determine its efficiency and the possibility of concentrating the extract. Five bottles, containing two pounds of stems each, were placed one above the other; cold water was added to the upper one, and the solution was passed through the others in succession.

When the liquid from the first bottle gave faint response to the test for nicotine, the current was turned into the second, and soon through the whole. Altogether, two gallons of liquid were obtained. The alkalinity of this liquid was determined and enough sulphuric




SMOKE ABSORPTION APPARATUS

acid added to make it neutral. The purpose of this was to change the nicotine to the sulphate and thus render it less volatile. In all, 63·14 cubic centimetres of 95 per cent sulphuric acid were required. The extract was then boiled down. A considerable

amount of solid material separated so that the liquid was filtered while still hot. On cooling, a large quantity of crystals was produced, which, on testing, seemed to be mostly potassium nitrate. The liquid was evaporated and cooled several times, and several quantities of crystals were obtained, in all, 265 grams. To separate these required considerable manipulation, because of the large amount of extraneous matter. Also the liquid became very thick and burned on the bottom several times emitting a powerful odour of nicotine, in each instance causing considerable loss. At 350 cubic centimetres the liquid was a thick viscous syrup which could be scarcely poured. Analysis showed this to contain 22·85 grams of nicotine out of the possible 32·7, or about 70 per cent of that contained in the stems. The extract thus prepared contained 6·5 grams of nicotine per 100 cubic centimetres.

### 3. Extraction with a Hydrocarbon.

The method employed consisted in soaking the coarsely ground ns with an alkaline solution to liberate the nicotine, and shaking .th the hydrocarbon in a separating funnel; then draining off the solution and shaking it with dilute sulphuric acid to remove the nicotine. Just enough alkaline solution was used to soak the stems thoroughly. The results are contained in the following table:—

TABLE XI

| No | Weight of stems used. | Nicotine content | Alkali used. | Hydrocarbon used. | Times shaken. | Hydrocarbon obtained | Acid used | Nicotine obtained | Per cent of nicotine obtained |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 50 g | 0·53 g | NaOH solution | 200 cc gasoline | 1 | 175cc | 10cc $2nH_2SO_4$ | 0·0797g | 14 % |
| 2 | 100g | 1·07g | 200 cc 2% NaOH | 500 cc. coal oil. | 4 | | 50 cc $2nH_2SO_4$ | 0·8563g | 79·4% |
| 3 | 100g | 1·07g | 200 cc lime-water. | 500 cc. coal oil. | 8 | 415cc | 5Cc $2nH_2SO_4$ | 0·7054g | 65·7% |

In No. 1 it will be noted that the stems were only shaken once with gasoline, while in No. 2 they were shaken with gasoline and acid, alternately, four times in succession. In the case of No. 3, af..r the eighth time of shaking, the stems were shaken with coal oil and the oil with acid, and the latter tested for nicotine without result. A few cubic centimetres of 10 N. caustic soda were added

to the stems and the test repeated. A decided precipitate was obtained. Five hundred cubic centimetres of coal oil were then added, and the extraction continued, for three more shakings. An analysis gave 0·3488 gram more of nicotine, making 1·054 grams in all, or 98·5 per cent. The conclusion is that coal oil will serve as an extractor, though less efficient than gasoline; but limewater is too weak an alkali. The above results seemed to warrant a further investigation of this method, and as coal oil has the advantage of cheapness, and is safer to handle an l less volatile than gasolene, it was decided to employ it.

*To determine the absorptive power of coal oil.*—Fifty grams of stems were soaked with 100 cubic centimetres 2·5 per cent sodium hydroxide solution and shaken with 500 cubic centimetres coal oil. The oil was drained off and an aliquot part pipetted for analysis. Then the oil solution was placed on 50 grams of fresh alkali-treated stems. This was repeated seven times, whereupon the amount of oil become too small for accurate analysis. The results are contained in Table XII.

TABLE XII.

| No. | Amount 2·5 per cent Sod. Hyd used. | Time of soaking | Oil Sol. used. | Oil Sol. obtained. | Time of extracting. | Wt. of Nic. per 100 cc. | Nicotine removed per 100 cc. |
|---|---|---|---|---|---|---|---|
| 1 | 100 cc | 5 min. | 500 cc | 475 cc | 10 min. | 0·0571 gm | 0·0571 gm. |
| 2 | 125 " | 5 " | 396 " | 362 " | 10 " | 0·1336 " | 0·0765 " |
| 3 | 110 " | 5 " | 285 " | 270 " | 10 " | 0 1964 " | 0·0628 " |
| 4 | 115 " | 3 h. 45 m. | 195 " | 170 " | 2 h. | 0·3182 " | 0·1218 " |
| 5 | 130 " | 30 min. | 150 " | 130 " | 1 h. 45 m | 0·3878 " | 0·0696 " |
| 6 | 125 " | 30 min | 112 " | 85 " | 45 min. | 0·4093 " | 0·0221 " |
| 7 | 125 " | 30 " | 75 " | 45 " | 30 " | 0·4416 " | 0·0317 " |

It will be noticed that a number of variables were introduced in the above series of experiments. The amount of alkaline solution (col. 2) was varied to determine its effect on the amount of oil solution obtained. Enough to soak the stems thoroughly seemed as effective as an excess. The mistake was made of varying both the time of soaking and time of extracting; so the effect of these cannot well be distinguished. Because of the number of variables introduced, the above experiment is not very conclusive; but seems to show that, after the oil reaches a concentration of about 0·4 gram of nicotine per 100 cubic centimetres, it is not a

very efficient solvent of nicotine, i.e., is nearly in equilibrium with the alkaline solution present.

Coal oil shaken with a commercial 40 per cent nicotine solution contained, as an average of two analyses, 4·41 grams of nicotine per 100 cubic centimetres. This did not appear to indicate that coal oil is a very efficient solvent for nicotine, in the presence of water; but the presence of an alkali in the water alters the distribution considerably.

*To determine the effect of the time of soaking the stems on the yield of nicotine*:—In this experiment 25 grams of stems were soaked in 50 cubic centimetres of milk of lime (5 grams to 100 cubic centimetres) for half hour, extracted with coal oil for ten minutes, and the nicotine extract analysed. The experiment was repeated, with the difference that the stems were soaked 2½ hours. The results were:—

| Time of Soaking. | Nicotine Removed per 100 cc. |
|---|---|
| 30 minutes. | 0·1508 gram. |
| 2½ hours. | 0·1502 " |

It appears that soaking the stems 30 minutes is as effective as a longer period.

*To determine the effect of the time of extracting with coal oil on the yield of nicotine*;—In this experiment 200 grams of stems were moistened with 150 cubic centimetres 2 5 per cent sodium hydroxide solution and extracted with 500 cubic centimetres coal oil.

At the intervals indicated 25 cubic centimetres were withdrawn for analysis. The results are recorded, in tabular form, below:—

TABLE XIII.—Time of Extracting.

| Time. | Weight of Nicotine per 100 cc. oil. | Increase of Nicotine per 100 cc. oil. |
|---|---|---|
| 10 min. | 0·0657 gm. | 0·0657 gm. |
| 20 " | 0·0781 " | 0·0124 " |
| 45 " | 0·0710 " | |
| 1 hr. 10 min. | 0·0726 " | 0·0016 " |
| 2 " 10 " | 0·0790 " | 0·0064 " |
| 3 " 10 " | 0·0810 " | 0·0020 " |
| 21 hrs. | 0·0848 " | 0·0030 " |

Total oil solution recovered was 458 cubic centimetres. The conclusion from the above is that a condition of equilibrium is nearly reached in 20 minutes of extraction.

To confirm the above the experiment was repeated with other stems.

TABLE XIV.—Time of Extracting.

| Time. | Weight of nicotine per 100 cc. Oil. | Increase of nicotine per 100 cc. Oil. |
|---|---|---|
| 5 min. | 0·1086 gm. | 0·1086 gm. |
| 14 " | 0·2191 " | 0·1105 " |
| 29 " | 0·2241 " | 0·0050 " |

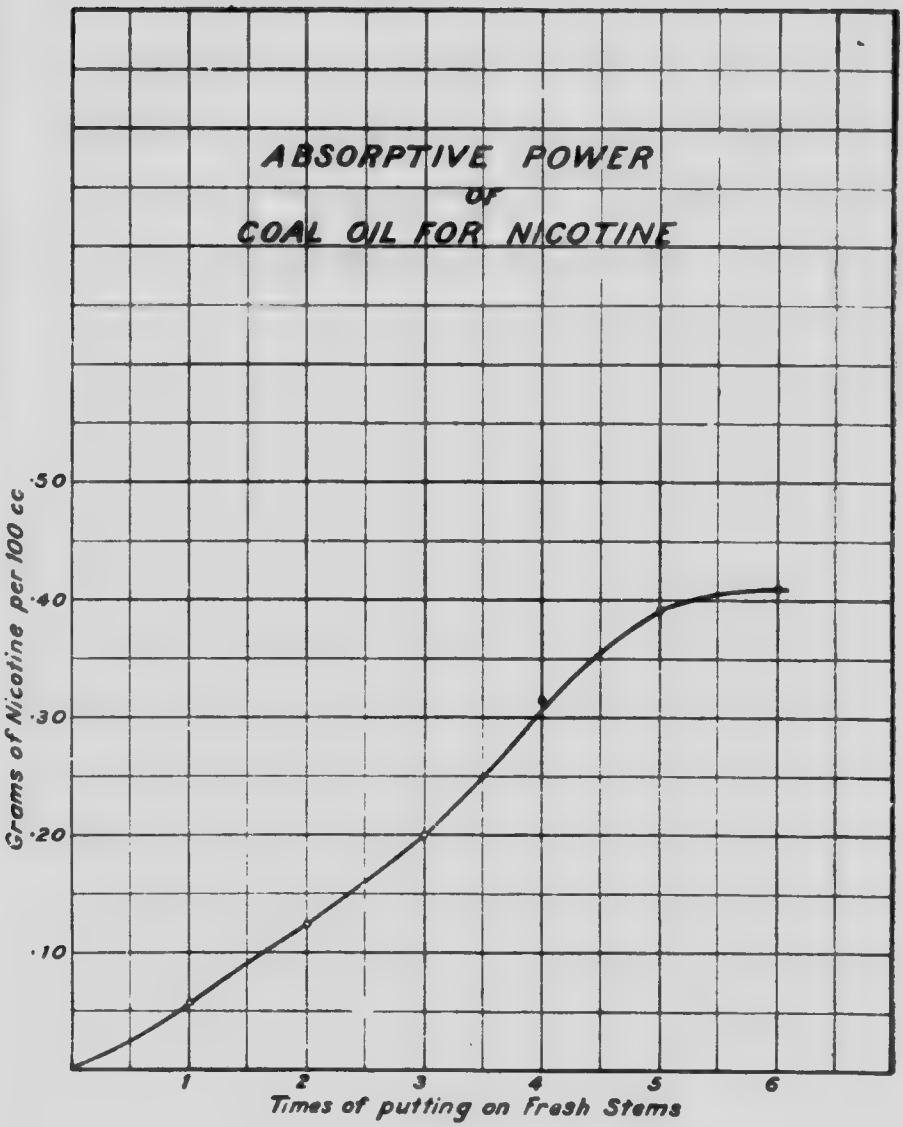
*Investigation as to the best alkali to use.*—In this experiment 25 grams of stems were placed in four different flasks and 50 cubic centimetres of alkaline liquid of the nature indicated in the table was added. They were then extracted for the same length of time with 100 cubic centimetres coal oil and the latter poured off and shaken with dilute acid, the nicotine from which was then precipitated.

TABLE XV.—Best Alkaline Solution.

| No. | Solution used. | Weight of Nicotine per 100 cc. |
|---|---|---|
| 1 | Dilute sodium hydroxide, 0·15 gm. per 100 cc | 0·0650 gm. |
| 2 | Sodium hydroxide 2·5 gm. per 100 cc. | 0·0942 " |
| 3 | Liquor from leaching stem ashes | 0·0343 " |
| 4 | Milk of lime | 0·0985 " |

It appears from the above that lime is the best alkali to use at the strength indicated.

*Removal of nicotine from oil solution.* It was found that vigorous shaking of the oil and acid caused an immediate removal of the nicotine from the former. An extraction of the baffle plate type proved effective, the result depending on the amount


ABSORPTIVE POWER
OF
COAL OIL FOR NICOTINE
Grams of Nicotine per 100 cc
.50
.40
.30
.20
.10
1
2
3
4
5
6
Times of putting on Fresh Stems

of nicotine in the oil and its rate of passage through the apparatus. An extractor 2 centimetres in diameter and 40 centimetres long, containing twelve baffle plates removed all the nicotine from a solution containing 0·2 grams per 100 cubic centimetres, when passed at the rate of 25 cubic centimetres per minute. Another effective method was to spray the oil solution into the acid, under pressure, through a fine nozzle.

To determine whether an acid solution approaching neutralization would extract the nicotine, 100 cubic centimetres of a 12 per cent acid solution was neutralized with nicotine and 5 cubic centimetres more of 2 N acid added. The solution was then tested in the extractor and removed the nicotine as effectively as a 12 per cent solution.

*Loss of Coal Oil*—From columns 4 and 5, table XII, we see that as an average of seven experiments, 50 grams of stems retained 25 cubic centimetres of coal oil. In the experiments on the time of extracting, 200 grams of stems retained 42 cubic centimetres of coal oil.

A further experiment was undertaken, using 900 grams of stems thoroughly soaked with alkaline solution (2500 cubic centimetres per 1000 grams). Only 125 cubic centimetres were retained. So it appears that, the greater the quantity of stems used the less the loss of coal oil. The stems were merely allowed to drain in the above experiments.

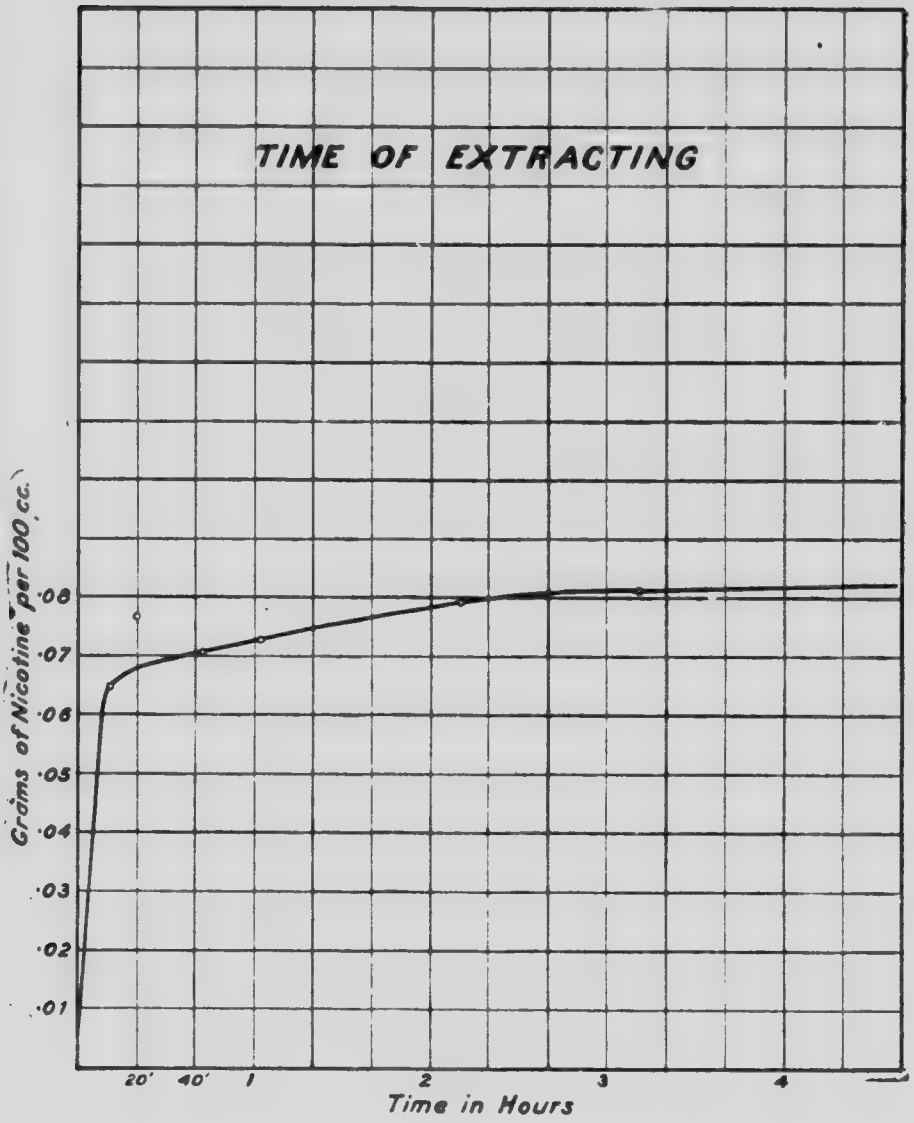
*Other facts observed*:—The amount of alkaline solution necessary to soak 100 grams of stems was 200 cubic centimetres.

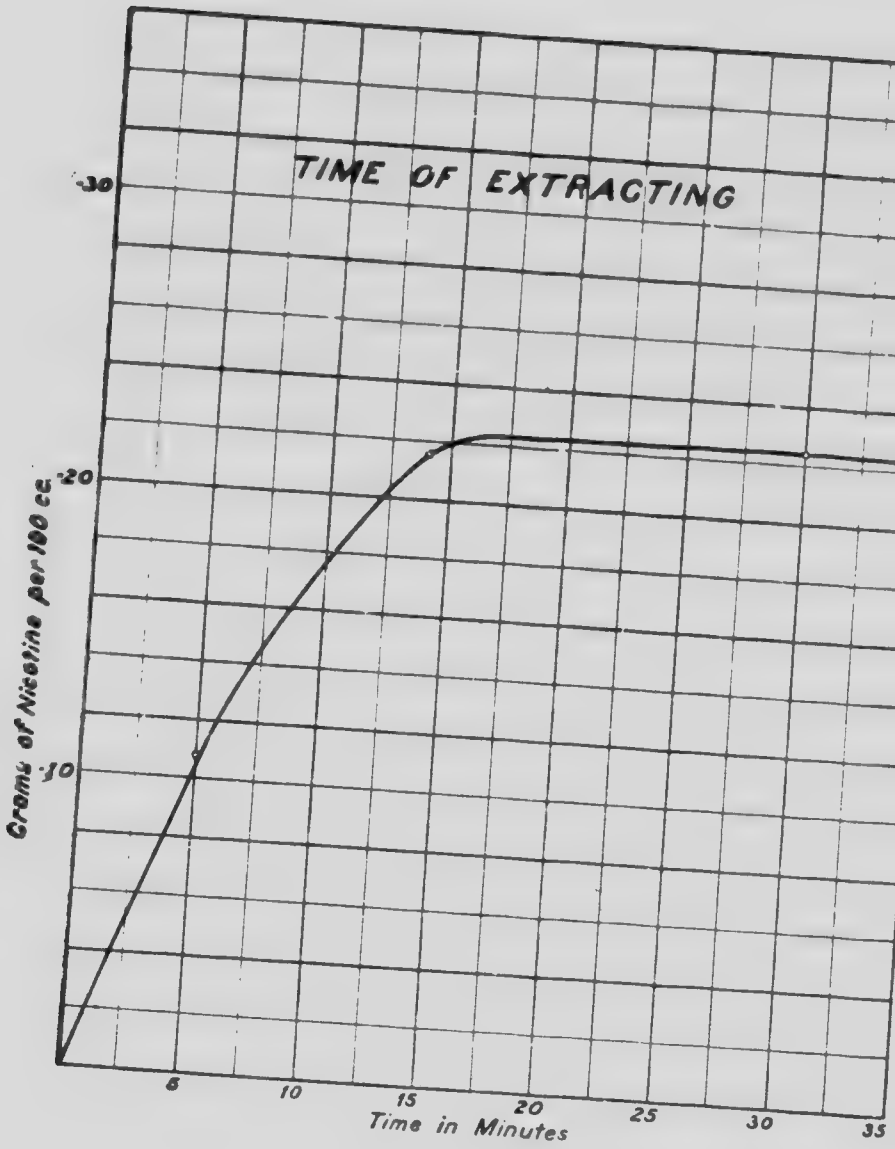
The volume of 100 grams of soaked stems was 450 cubic centimetres.

To cover 100 grams of soaked stems required 200 cubic centimetres of coal oil.

## EXTRACTION WITH HYDROCARBON ON A 10-POUND SCALE.

The above observations were made the basis of an experiment on a 10-pound scale. Five bottles of capacity $1\frac{1}{10}$ gallons were nearly filled with 10 pounds of coarsely ground stems (containing about 32·7 grams nicotine in all), 2 pounds of stems to the bottle. One-third of a gallon of water, containing 2 ounces of slaked lime, was then added to each. The bottles were placed


TIME OF EXTRACTING
Grams of Nicotine per 100 cc.
·08
·07
·06
·05
·04
·03
·02
·01
20'
40'
1
2
3
4
Time in Hours


TIME OF EXTRACTING
.30
.20
.10
Grams of Nicotine per 100 cc
5
10
15
20
25
30
35
Time in Minutes

one above the other, and the bottom of one connected to the top of the next, etc. After standing half hour, coal oil was passed through these in succession. The oil was then passed through two extractors of the baffle-plate type, connected in series, and containing between them 250 cubic centimetres of 12 per cent sulphuric acid. As, however, a test of the first portion of oil passed through these showed that it retained considerable nicotine, shaking the oil with the acid was substituted. After the removal of the nicotine by this method, the oil was run through again. Each bottle was provided with a tube and tap for withdrawing a sample for analysis. When the upper bottle was completely extracted, as shown by analysis, it was removed and the current was started at the second, and so on.

Five gallons of oil were employed. A small amount (say 100 cubic centimetres) was lost in effecting the removal of the extractor, and a considerable amount more was lost due to leaks arising from the softening of the rubber connections during the run. I have no means of estimating the latter as the leak was probably not discovered at once and the oil disappeared down a crack. Four and a quarter gallons of oil were recovered. The reader is reminded that the stems retain some of this.

The total oil passed through the apparatus, including that used again, was $10\frac{3}{4}$ gallons. Thus this amount would have to be pumped for the 10 pounds. Of course a continuous extraction method whereby a fresh bottle would be added at the end of the series when one was removed from the beginning, would be much more efficient.

Analysis showed 24·9 grams of nicotine in 250 cubic centimetres of acid solution, or an extraction of 76 per cent of that present in the stems.

### 4. Steam Distillation.

The work of those who have developed the methods of tobacco analysis shows that all the nicotine may be extracted by distillation with steam.

Typical examples from my analyses of the amounts of distillate obtained are:—

| Weight of tobacco used. | Distillate obtained. |
|---|---|
| 25·94 grams stems | 500 cubic centimetres. |
| 18·36 grams scrap | 500 " " |
| 16·36 grams scrap | 500 " " |

From this one would be safe in concluding that a distillate of 500 cubic centimetres would contain practically all the nicotine in 25 grams of stems. A method of extracting nicotine by steam distillation was suggested by German patent 254,667, June 6, 1911, which prescribes the addition of an alkali, distilling with steam, and passing the vapours through absorption vessels, charged with acid, which is to be kept at a high enough temperature to prevent the condensation of the steam. The steam is then to be used over again.

I first satisfied myself that the method is feasible, by boiling water in a flask and passing the resulting steam through a solution of sulphuric acid kept at the boiling point of water. The steam was then returned to the flask by means of an atomizer bulb the temperature being reduced until just sufficient to prevent condensation. In this manner, a circulation was established without much difficulty.

A nicotine solution was next made alkaline and boiled, and the resulting vapour passed through a 10 per cent solution of sulphuric acid, kept at a high enough temperature to prevent its condensation. The vapour was then condensed and tested for nicotine, without result.

Next, 50 grams stems were mixed with 20 grams lime and placed in two flasks (25 grams in each) connected in series to a steam generator. They were kept heated and a current of steam passed through. The steam was then passed through 100 cubic centimetres of water containing 5 cubic centimetres of 95 per cent sulphuric acid. The steam was tested for nicotine from time to time, before and after passing through the acid. After the steam from approximately 300 cubic centimetres of water had been passed

through, although the steam before passing gave a distinct test, the distillation was stopped, as other experiments showed the possibility of extracting all the nicotine by steam distillation, and it was desirable to determine whether most of this passed over in the first portion of the distillate. The acid solution showed no increase in volume and contained 0·156 gram of nicotine. The stems contained 0·365 gram. Thus 43 per cent had been extracted.

## Comparisons and Conclusions.

In comparing the above methods, there are four main factors to consider: (1) Efficiency, (2) purity of product (3) cost, (4) condition of stems after extraction.

*1. Efficiency.*—The best yields by the various methods were:—

| | |
|---|---|
| *Small Experiments* — | |
| 1. Smoke absorption | 76 % |
| 2 Acid extraction. | 78·6% |
| 3 Water extraction. . | 70·5% |
| 4 Extraction with hydrocarbon. | 98·5% |
| 5 Steam distillation.. | 100 % |
| *10 pounds Scale Experiments* — | |
| Water extraction. . | 70% |
| Oil extraction.... | 76% |

In my small scale acid and water extraction, only one extraction was carried out. By three successive extractions with water, Edwardes-Ker obtained over 96 per cent of the nicotine.

The smoke absorption methods appears to be the least efficient. It occured to me later that its efficiency might be increased by mixing the tobacco with lime, before burning.

Of the other methods, steam distillation is most efficient; then the extraction with hydrocarbon, and, lastly, water extraction. I see no reason, however, why, by concentrating on and perfecting any one of these methods, practically all the nicotine might not be obtained.

*2. Purity of Product.*—There is little difference between the products of steam distillation and extraction with hydrocarbon so far as appearances and freedom from sediment are concerned. That from the former undoubtedly contains considerable ammonium sulphate.

The product from the smoke absorption experiments was very dark and of strong odour, but contained little sediment.

Water and acid extraction yielded a solution full of sediment and extraneous matter, extremely difficult to concentrate and purify.

*3. Cost.*—It is probable that there would be little difference in initial outlay for conducting the water, coal oil and steam extractions. While very simple apparatus could be used for all, some form of continuous extraction apparatus, such as is employed in the extraction of sugar from sugar-beets, would be most desirable. The two latter would require absorption towers; while the first would require an evaporation and filtration plant. In the steam distillation, if carried on as suggested, some arrangement would be needed to keep the extractors and towers heated. Such arrangements are employed in a beet sugar battery. The two latter methods would require a pump to keep up the circulation.

The cost of raw material per ton of stem would be:—

WATER EXTRACTION.

| | |
|---|---|
| 1 ton stems. | |
| Sulphuric acid, 50 pounds | $10 $15 00 |
| Coal, ¼ ton | 1 75 |
| | 2 50 |
| | $19 25 |

The above calculation is made on the basis of war-time prices. In arriving at the last item, it was calculated that, on the basis of 2 gallons of solution from 10 pounds of stems, 1 ton would yield 400 gallons, or about 2 tons of solution. According to Thorpe, a simple multiple effect system evaporates 8½ pounds of water per pound of coal. So the above would require about 500 pounds or ¼ ton of coal.

EXTRACTION WITH HYDROCARBON.

| | |
|---|---|
| 1 ton stems. | |
| 100 pounds lime | $10-$15 00 |
| 12 pounds sulphuric acid | .30 |
| 27 gallons coal oil lost at 18 cents | 50 |
| | 4 86 |
| | $20 66 |

The lime was calculated on the basis of an excess over that required to displace both the ammonia (2 per cent) and nicotine (1 per cent). The sulphuric acid is twice that needed for the

nicotine, alone as a special experiment showed that the oil solution neutralized nearly twice the acid required for the nicotine alone, showing that some other alkaline substances are dissolved in addition to the nicotine.

The coal oil lost is calculated on the basis of 125 cubic centimetres to 900 grams of stems. This is safe assumption, as in my experiments the stems were not pressed out. My results, too, seem to show that the oil retained per pound of stems falls off when the weight of stems is increased.

STEAM DISTILLATION.

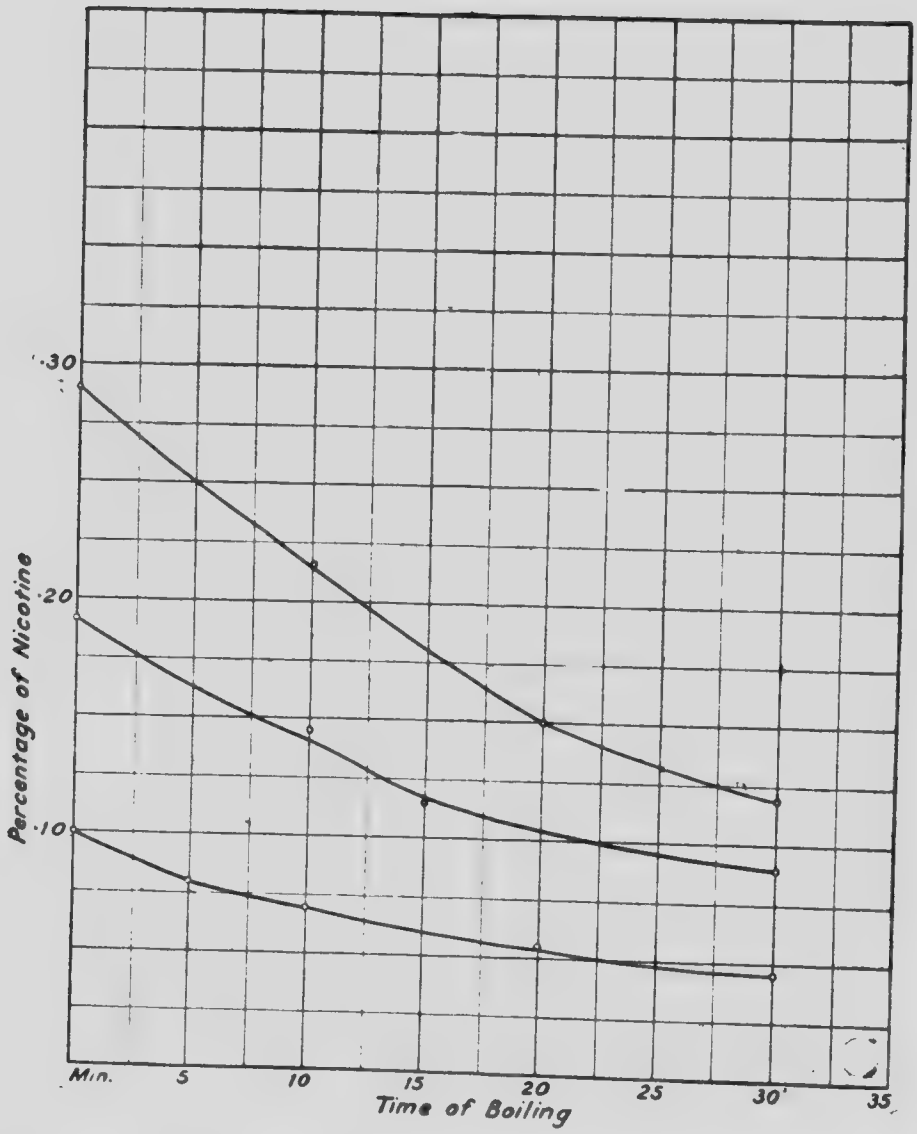
| | | |
|---|---|---|
| 1 ton stems | $10 | $15 00 |
| 100 pounds lime | | .30 |
| 50 pounds sulphuric acid | | 1 75 |
| ½ ton (?) coal | | 5 00 |
| | | $22 05 |

The sulphuric acid used is taken to be the same as for the water extraction.

The coal is required for generating the steam and keeping the apparatus heated. With the data available it is difficult to arrive at an estimate of this. If we proceed in the basis of 500 cubic centimetres of water for 25 grams of stems, a calculation shows that about 2½ tons of coal are required per ton of stems. This does not include the cost of keeping the apparatus heated. If we consider that five or more extraction vessels in series are used instead of one, and the steam used over again, we shall probably be safe in reducing the amount of coal required to one fifth of 2½ tons, or half ton.

The Cost of Manipulation would probably be greatest in the steam distillation method due to the necessity of keeping the apparatus heated and of controlling temperature and steam pressure. The coal oil extraction would have the lowest cost, being easy to manipulate and control. In the water extraction, the cost of evaporation and purification would be considerable. The cost of grinding stems would be common to all

*4. Condition of Stems after Extraction.*—The oil extraction seems to leave the stems in the best condition for the recovery of all the valuable ingredients. On standing after extraction, a powerful odour of ammonia developed. This ammonia could be easily


·30
·20
·10
Percentage of Nicotine
Min.
5
10
15
20
25
30'
35
Time of Boiling

recovered while drying the stems. The dried stems could be burned any oil retained aiding in this, and the heat generated could propably be used to dry a further quantity of stems. The potash could easily be leached from the ashes, which would contain a large percentage of lime and phosphoric acid and would thus have a value as fertilizer.

Or the extracted stems might be used directly as a fertilizer, if the oil remaining did not interfere.

The steam distillation method leaves the stems in a dry condition very suitable for use as a fertilizer. A large part of the nitrogen would be driven off as ammonia. This would be caught in the acid but might prove difficult to separate from the nicotine sulphate. The water extraction method removes a large amount of potash and nitrogen and thus leaves the stems with greatly decreased fertilizing value. However, during the concentration of the solution most of the dissolved material might be recovered in a very desirable form, though the recovery would involve considerable manipulation.

*Conclusion.*—Taking all factors into consideration the extraction with hydrocarbon seems most promising, especially if the loss of the hydrocarbon can be considerably reduced. It shares with steam distillation the advantage of producing a solution of any desired strength, depending the strength of acid used. It also readily lends itself to scale extraction, without very complicated machinery. However, it would be advisable to try both this and the steam distillation methods on a 100-pound scale, before coming to a final conclusion.

## Concentrating the Nicotine Solution.

Boiling nicotine solution at ordinary pressure leads to loss of nicotine as the latter is volatile with steam. This is shown by accompanying curves plotted by M. Edwardes-Ker. If the nicotine be first changed to sulphate and care exercised in the evaporation, the loss may be avoided. It was found that in evaporating a slightly acid solution of nicotine sulphate in a flask over a sand bath, the vapours contained a considerable amount of nicotine when strong heat was applied, but with a gentle heat they were free from nicotine. It seems probable that the nicotine was pro-

duced by the decomposition of the sulphate on the hot sides of the flask.

Another method of concentration consists in removing the nicotine from the alkaline solution by gasolene, and removing the nicotine from the latter by sulphuric acid. A modification of the use of hydrocarbon in extracting nicotine from tobacco consists in first extracting with water and then obtaining a concentrated solution by this method.

## VALUE OF TOBACCO WASTE AS A FERTILIZER AND SOURCE OF POTASH.

My attention was soon directed to the large percentage of potash and ammonia in the stems. At the present time, the importance of this almost overshadows their value as a source of nicotine.

In a letter, dated November 6, 1917, Dr. E. H. Jenkins, Director of the Connecticut Agricultural Experimental Station, furnished the following analysis, which is the average of thirteen analyses made at the station.

AVERAGE OF THIRTEEN ANALYSES OF TOBACCO STEMS.

| | |
|---|---|
| Water | 20.70 |
| Organic and volatile (including nitrogen 2·05 per cent) | 63.89 |
| Sand | 1.57 |
| Potash | 7.54 |
| Soda | 0.18 |
| Lime | 3.84 |
| Magnesia | 0.53 |
| Oxide Iron | 0.11 |
| Phosphoric Acid | 0.60 |
| Sulphur | 0.50 |
| Chlorine | 0.54 |
| | 100.00 |

A rough experiment of my own gives some idea of the potash content of Canadian waste stems and of the ease of extracting it.

The ash (24·4 grams) from 100 grams of stems was leached with 50 cubic centimetres of boiling water and washed till the wash water showed no alkalinity with litmus paper. Three hundred cubic centimetres were obtained. An aliquot part was titrated against N/10 sulphuric acid, first using phenol phthalein and

finishing with methyl orange, and showed that nearly 10 grams of potassium carbonate and 0·33 gram of potassium hydroxide had been extracted. Evaporation, during which a small amount was lost by sputtering, left 10·01 grams of a pure white residue. The above analysis shows that this was probably about 98 per cent potash and 2 per cent soda.

In the water extraction of the stems, over ½ pound of crystals, apparently mostly potassium nitrate, were obtained from 10 pounds of stems.

That the stalks (not to be confused with the stems which are the midribs of the leaves) are also valuable as a fertilizer, or as a source of potash, is indicated by the following table of ash analysis, taken from the report of the Connecticut Agricultural Experimental Station, 1884.

ANALYSIS OF ASH FROM TOBACCO STALKS.

| | |
|---|---|
| Sand, silica and matter insoluble in acid | 3.17 |
| Oxide iron and alumina | .30 |
| Lime | 8.53 |
| Magnesia | 5.15 |
| Potash | 43.93 |
| Soda | 0.35 |
| Phosphoric acid ($P_2O_5$) | 5.95 |
| Sulphuric acid ($SO_3$) | 6.14 |
| Chlorine | 9.09 |
| Carbonic acid | 14.80 |
| Carbon | 3.16 |
| | 100.57 |

H. W. Haskins has calculated that the fertilizing material from an acre of stalks is:—

| | |
|---|---|
| Nitrogen | 87·23 pounds. |
| Potash | 132·85 " |
| Phosphoric acid | 20·92 " |

This is worth about $24 per acre (1913) or $8.40 per ton of partially dried stalks (50-53 per cent water). The usual plan is to throw these on the land in the autumn, leave exposed during the winter, and burn in the spring. Analysis showed that 50 per cent of the nitrogen is lost by this treatment. This amounts to 40 pounds valued at $7. Considerable valuable organic matter is also destroyed. He recommends that the stalks be chopped up and buried.

The above indicates that tobacco waste is too valuable at the present time as a source of potash, or as fertilizing material to be shipped out of the country. The United States has placed tobacco scrap under an embargo for this reason.

## RETURNS FROM ONE TON OF STEMS.

If we count on an average of 1 per cent nicotine at $2.25 per pound wholesale, the return would be $45 per ton, or over twice the cost of raw material and chemicals used in the hydrocarbon process. A conservative estimate of 75 per cent extracted would yield $33.75 or $13 more than the cost of material.

With potassium carbonate at the present (April, 1918) price of 85 cents per pound of 90-95 per cent pure, and with a yield of 200 pounds from one ton of stems, extracting both the nicotine and potash would be a very paying proposition. No better opportunity could be chosen for starting. Good returns are assured and will not depend upon the abnormal demands of war.

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